SUNWAY UNIVERSITY

# The energies of non-standard intermolecular interactions are competitive with conventional hydrogen-bonding

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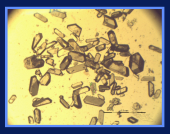
Research Centre for Crystalline Materials

AsCA 2018 CRYSTAL 32
December 2-5 2018 | Auckland, New Zealand

## Crystals?

Why do crystals form?

How do crystals form?



## Crystal Engineering

- Determine how Molecules pack
- Design specific architectures
- Optimise for applications

## Intermolecular Interactions

Well known…

Hydrogen-bonding (HB)
Halogen-bonding (HB)

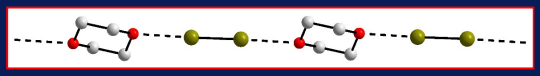
$A-H\cdots B$ $\quad$ $A-X\cdots B$

## Intermolecular Interactions

Well known…

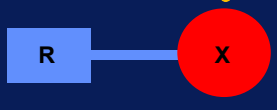
Hydrogen-bonding (HB)
Halogen-bonding (HB)

Odd Hassel
1897 – 1981



## Halogen-bonding

**Halogen-bond acceptor** **Nucleophilic**




**Electrophilic**
**Halogen-bond donor**

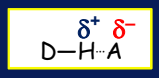
**Anisotropic**

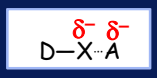
Polar cap, σ-hole

## Intermolecular Interactions

Well known…

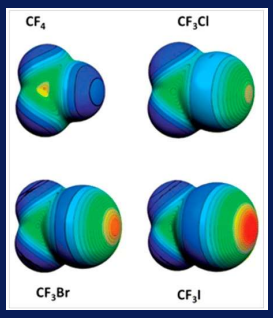
Hydrogen-bonding (HB)
Halogen-bonding (HB)




$(HB)^2$: Similar in energy = 5 – 15 kcal/mol

## σ-hole




Halogen-bonding

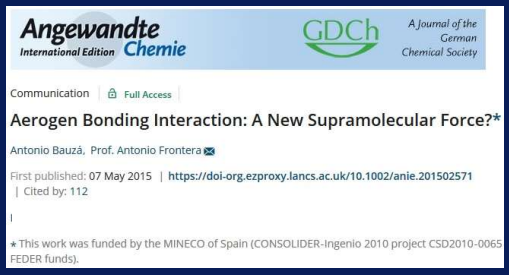
Chalcogen-bonding

Pnicogen-bonding

Tetrel-bonding

Aerogen-bonding

Clark, T.; Hennemann, M.; Murray, J. S.; Politzer, P.
Halogen Bonding: The Sigma-Hole *J. Mol. Model.* **2007**, *13*, 291– 296


Angewandte International Edition Chemie
GDCh A Journal of the German Chemical Society

Communication | Full Access

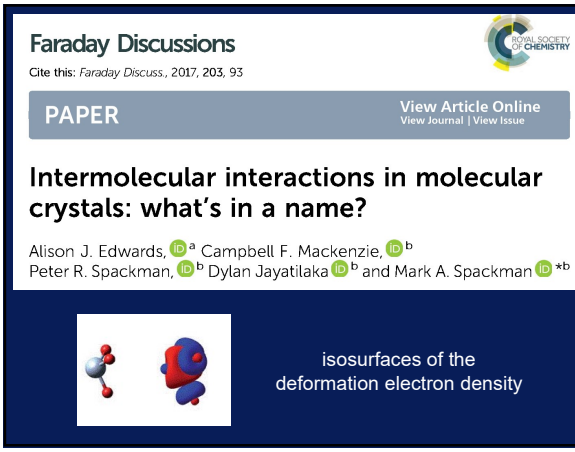
**Aerogen Bonding Interaction: A New Supramolecular Force?***

Antonio Bauzá, Prof. Antonio Frontera

First published: 07 May 2015 | https://doi-org.ezproxy.lancs.ac.uk/10.1002/anie.201502571
| Cited by: 112

* This work was funded by the MINECO of Spain (CONSOLIDER-Ingenio 2010 project CSD2010-0065 FEDER funds).

…favorable noncovalent interaction between a covalently bonded atom of Group 18 (known as noble gases or aerogens) and a negative site, for example, a lone pair of a Lewis base or an anion.


Faraday Discussions

Cite this: *Faraday Discuss.*, 2017, **203**, 93

PAPER View Article Online
View Journal | View Issue

**Intermolecular interactions in molecular crystals: what's in a name?**

Alison J. Edwards, [a] Campbell F. Mackenzie, [b]
Peter R. Spackman, [b] Dylan Jayatilaka [b] and Mark A. Spackman *[b]



isosurfaces of the deformation electron density


Issue 9, 2009 Previous Article Next Article

From the journal: Chemical Society Reviews

**How molecules stick together in organic crystals: weak intermolecular interactions**

Jack D. Dunitz*[a] and Angelo Gavezzotti*[b]



…most organic molecules feature hydrogen atoms at the periphery and so that C–H···X interactions are inevitable

*Chem. Soc. Rev.*, **2009**,*38*, 2622-2633



## Prevalence of Space Group Adoption

CSD: 865,342 entries

| | | |
|---|---|---|
| $P2_1/c$ | 279041 | 34.5 |
| $P\bar{1}$ | 198014 | 24.7 |
| $C2/c$ | 67434 | 8.4 |
| $P2_12_12_1$ | 58438 | 7.2 |
| $P2_1$ | 41791 | 5.2 |
| $Pbca$ | 26951 | 3.3 |

Six close-packing SG's account for >83% of structures

## How significant are non-covalent interactions: tetrel-bonding

ChemPubSoc Europe
DOI: 10.1002/chem.201804676
CHEMISTRY A European Journal Full Paper
Sn Interactions

**S···Sn Tetrel Bonds in the Activation of Peroxisome Proliferator-Activated Receptors (PPARs) by Organotin Molecules**

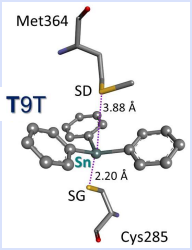
Antonio Frontera and Antonio Bauzá*[a]

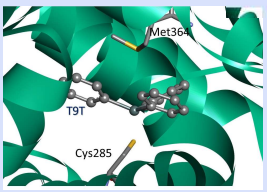
**Abstract:** In this study, a PDB (Protein Data Bank) analysis and theoretical calculations (PBE0-D3/def2-TZVP level of theory) were combined to analyze the impact of S···Sn tetrel-bonding interactions in the activation mechanism of peroxisome proliferator-activated receptors (PPARs) by two organotin derivatives, triphenyltin (TPT) and tributyltin (TBT). The presence of a covalently bonded CYS285 to the organotin molecule was found to be key to enhance the σ-hole-donor ability of the tin atom, thus strengthening the tetrel-bonding interaction with a sulfur atom belonging to a vicinal methionine residue (MET364).

*Chem. Eur. J.* **2018**, *24*, 16582–16587

## Tetrel-bonding in biology

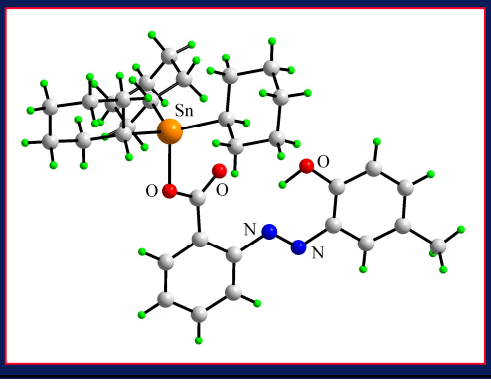

**pdb 3jw5**
PPARγ &**T9T**




Ignez Caracelli

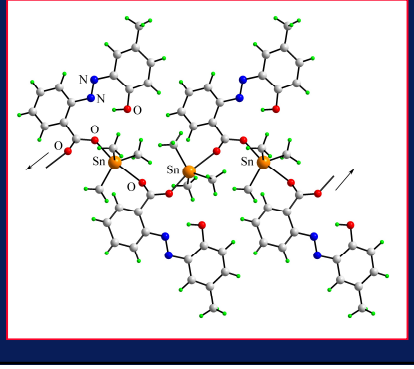
## $Cy_3Sn(O_2CR')_2$



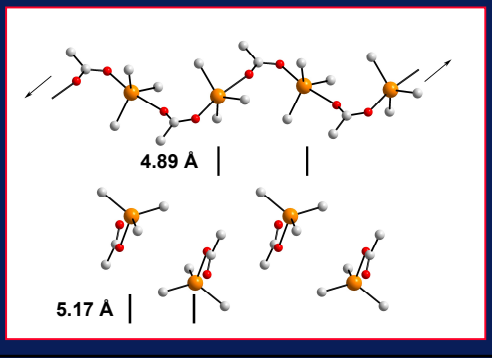

## Systematic analysis of $R_3Sn(O_2CR')$

| R | $^{117}Sn$ solution | $^{117}Sn$ solid-state |
|---|---|---|
| Cy | -8.5 | 23.7 |
| Me | 24.7 | 148.1 |

## $Me_3Sn(O_2CR'')$




## $R_3Sn(O_2CR'')$



## Tetrel-bonding: energy


THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

**Systematic Elucidation of Factors That Influence the Strength of Tetrel Bonds**

Steve Scheiner*

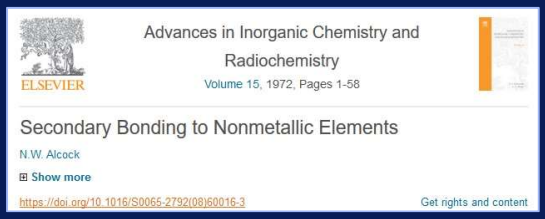
Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, United States

$(HB)^2$: Similar in energy = 5 – 15 kcal/mol

T = C, Si, Ge & Sn

| | |
|---|---|
| n = 0 | 0.9 kcal/mol |
| n = 1* | 6 – 9 kcal/mol |
| $SnF_4$ | 25.5 kcal/mol |

## Tetrel-bonding?


ELSEVIER

Advances in Inorganic Chemistry and Radiochemistry

Volume 15, 1972, Pages 1-58

Secondary Bonding to Nonmetallic Elements

N.W. Alcock

Show more

https://doi.org/10.1016/S0065-2792(08)60016-3

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## Tetrel-bonding?

Biological systems

Supramolecular association in crystals -
- holding molecules together
- moderation by steric effects
- influence upon coordination geometry

Energies of stabilisation comparable to $(HB)^2$

Well documented in the literature -
- Secondary-Bonding

## Gold Chemistry

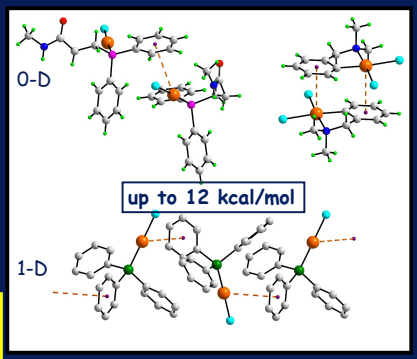
Competition between

i) Au···Au and hydrogen-bonding

Comparable in energy to HB

Schmidbaur, *Nature* **413** (2001) 31.

## Intermolecular Au···π(arene) interactions





*RSC Advances* **5** (2015) 41401.

## Gold Chemistry

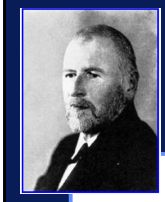
Competition between

i) Au···Au and hydrogen bonding

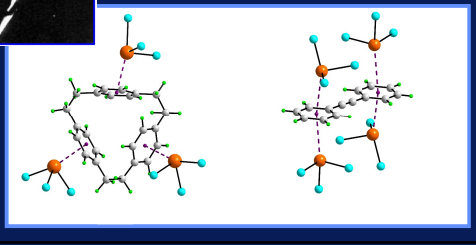
ii) Au···Au and Au···π(arene)

$(HB)^2$: Similar in energy = 5 – 15 kcal/mol

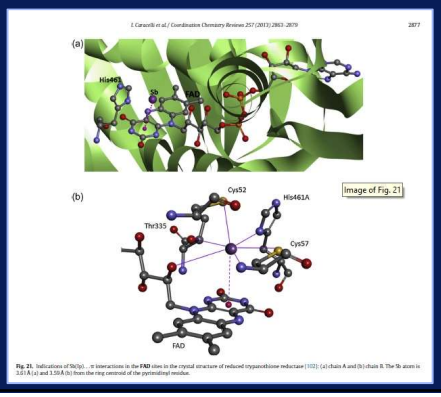
## Intermolecular M(lp)···π(arene) interactions



"Menšutkin complexes"



## Biology?




## Energy?

ChemComm

COMMUNICATION

View Article Online

On the nature of the stabilisation of the E···π pnicogen bond in the $SbCl_3$···toluene complex†

Rabindranath Lo,[a] Petr Švec,[b] Zdeňka Růžičková,[b] Aleš Růžička[b] and Pavel Hobza*[ac]

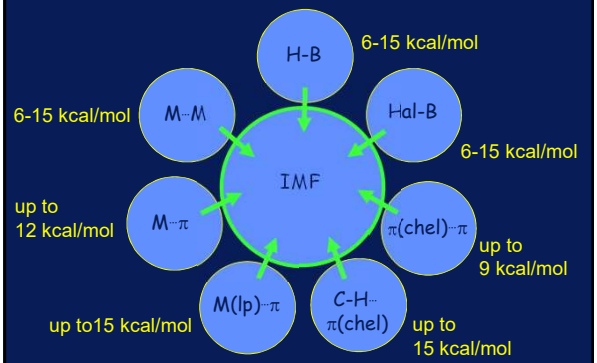
Cite this: *Chem. Commun.*, 2016, 52, 3500

Received 17th December 2015, Accepted 27th January 2016

DOI: 10.1039/c5cc10363k

| | | |
|---|---|---|
| $SbCl_3$ + | $C_6H_6$ | 7.7 kcal/mol |
| | $C_6H_5Me$ | 9.6 kcal/mol |
| | $C_6Me_6$ | 15.5 kcal/mol |

## Overview



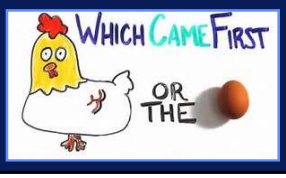

## Conclusions

More to supramolecular life than $(HB)^2$

"Emerging" interactions are competitive

Global molecular packing

"Egg Causality Dilemma"




## Sunway University


Fortuna Eruditis Favet ("*Fortune favours the prepared mind*")